

Effect of metal phthalocyanines on the synthesis and physicochemical properties of polyaniline

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DMSO and aniline provided by Sigma-Aldrich were purified by standard methods. After the process, all of their physicochemical constants corresponded to the referenced data. Hydrochloric acid, ammonium peroxodisulfate (APS), metal (Co^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Fe^{2+}) phthalocyanines (Aldrich) were used without any extra purification.

UV-vis spectra were recorded on a 2600 Shimadzu spectrophotometer in DMSO solution at 25°C, wavelengths ranging from 190 to 800 nm (slit width 2.0 nm, fast scanning speed) using a 1 cm thick quartz cuvette. The microstructure of nanoparticles was studied with a TESCAN MIRA 3 LMH high-resolution scanning electron microscope (SEM) equipped with a detector of scattered and backward scattered electrons. The survey was conducted at 10 kV accelerating voltage and 10^{-3} PA vacuum. Electrochemical studies of the samples were carried out using Elinse P30-JM potentiostat/galvanostat in a three-electrode system with a silver chloride reference electrode, a platinum wire as the auxiliary electrode, and ITO glass coated with a DMF solution polymer film as the working electrode. The electrical conductivity of the samples was measured by the four-probe method at room temperature using a KEITHLEY 2400 Source Meter.

Polyaniline (*I*) was obtained by chemical oxidative polymerization of aniline (1 g, 0.01 mol) in 0.2 M aqueous solution of hydrochloric acid (50 ml). A 0.125 M solution of APS (2.85 g, 0.0125 mol) in hydrochloric acid (50 ml) was added to the aniline solution. The reaction was performed with stirring for 24 hours at room temperature. The precipitate was washed with 1M hydrochloric acid to remove any by-products. Yield 0.74 g (81.0 %).

Polyaniline synthesis in the presence of metal phthalocyanine catalysts was performed similarly to the synthesis of *I*. The metal (Co^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Fe^{2+}) phthalocyanines (0.01 g L^{-1}) were added in 50 ml of 0.2 M hydrochloric acid solution of aniline (1 g, 0.01 mol). Then, a solution of APS (2.85 g, 0.0125 mol) in 50 ml of 0.2 M hydrochloric acid was slowly added to the aniline solution with metal (Co^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Fe^{2+}) phthalocyanines. The reaction mixture was kept for 1 hour at room temperature with continuous stirring. The precipitate was washed to a neutral medium with distilled water and dried in vacuum at 40°C. Yield of polymers 1-6 are presented in the Table S1.

Table S1 The polymer yield depending on the nature of the catalyst ([MPc] = 0.01 g L⁻¹, the reaction time was 1 h).

Polymer	Catalyst	Yield, g	Yield, %
1	-	0.74	81.0
2	CoPc	0.88	96.9
3	MnPc	0.82	90.1
4	ZnPc	0.87	96.4
5	NiPc	0.80	88.7
6	FePc	0.79	86.9